

## Communication

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# Two-dimensional covalent crystals by chemical conversion of thin van der Waals materials

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**ABSTRACT:**

Most of the studied two-dimensional (2D) materials have been obtained by exfoliation of van der Waals crystals. Recently, there has been growing interest in fabricating synthetic 2D crystals which have no layered bulk analogues. These efforts have been focused mainly on the surface growth of molecules in high vacuum. Here, we report an approach to making 2D crystals of covalent solids by chemical conversion of van der Waals layers. As an example, we use 2D indium selenide (InSe) obtained by exfoliation and converted it by direct fluorination into indium fluoride (InF<sub>3</sub>), which has a non-layered, rhombohedral structure and therefore cannot be possibly obtained by exfoliation. The conversion of InSe into InF<sub>3</sub> is found to be feasible for thicknesses down to three layers of InSe, and the obtained stable InF<sub>3</sub> layers are doped with selenium. We study this new 2D material by optical, electron transport and Raman measurements and show that it is a semiconductor with a direct bandgap of 2.2 eV, exhibiting high optical transparency across the visible and infrared spectral ranges. We also demonstrate the scalability of our approach by chemical conversion of large-area, thin InSe laminates obtained by liquid exfoliation into InF<sub>3</sub> films. The concept of chemical conversion of cleavable thin van der Waals crystals into covalently-bonded non-cleavable ones opens exciting prospects for synthesizing a wide variety of novel atomically thin covalent crystals.

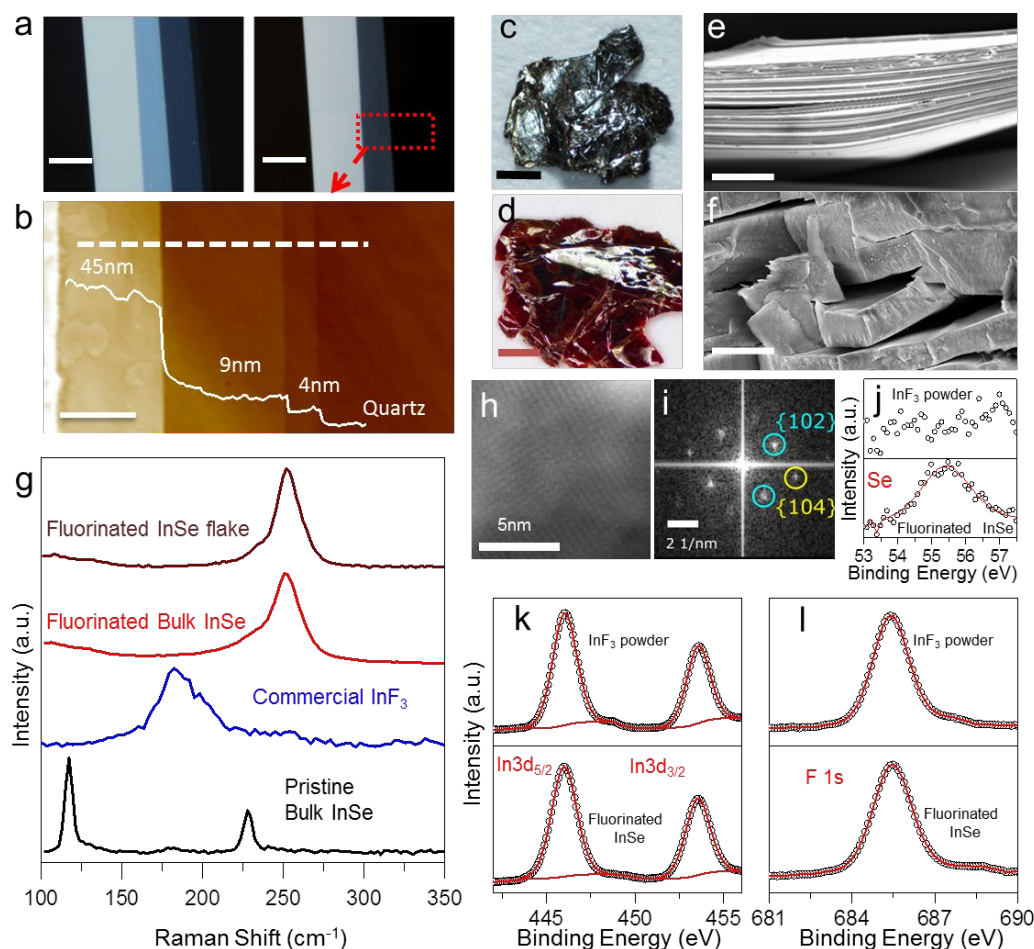
**KEYWORDS:** Indium Selenide, Fluorination, Indium Fluoride, 2D covalent crystal, van der Waals materials

Chemical modification of materials has proved to be a powerful tool for obtaining novel materials with desired and often unusual properties<sup>1-6</sup>. Following the exfoliation of graphene<sup>7</sup>, the family of

two-dimensional (2D) materials was populated either by direct exfoliation of layered bulk crystals<sup>7-10</sup> or by epitaxial growth techniques<sup>11-14</sup>. Also, the concept of using an existing 2D material as an atomic scaffold for synthesizing novel 2D materials has been demonstrated by hydrogenated and fluorinated graphene, called graphane<sup>5</sup> and fluorographene<sup>6</sup>, respectively. Similarly, ion exchange was used to modify existing 2D materials and synthesize MoS<sub>2</sub>, WS<sub>2</sub>, Cu<sub>2</sub>SnS<sub>3</sub>, ZnS, PbS, etc. However, these techniques are usually limited to producing 2D layers of the known layered crystals<sup>15-17</sup>. In contrast to layered crystals, where atomic layers are held together by weak van der Waals forces and hence can be separated by “brute” mechanical action, covalent solids cannot be exfoliated. One can also imagine the chemical conversion of two or more atomic layers of a van der Waals solid into a 2D covalent material of controlled thickness. Despite the simplicity and significance of creating a new class of materials, namely 2D covalent solids, this concept has not yet been explored for atomically thin layers of van der Waals crystals. Here, we successfully demonstrate the validity of this approach by reporting the chemical conversion of three or more layers of InSe into covalent InF<sub>3</sub> thin films by fluorination of layered 2D crystals of InSe.

We used the mechanical exfoliation method to prepare InSe flakes on a quartz substrate<sup>6, 18, 19</sup>. Exfoliated InSe flakes and bulk InSe crystals were then fluorinated by direct exposure to Xenon difluoride (XeF<sub>2</sub>) at elevated temperature using a method reported earlier<sup>6</sup> (see methods). Figure 1a shows the optical micrographs of InSe flakes before and after the fluorination process. After fluorination, the optical contrast from the thinner InSe flakes decreases significantly, but atomic force microscopy (AFM) confirms the preservation of the flake morphology and its 2D structure (Figure 1b). Using this method, we have fluorinated InSe flakes down to three-layer thicknesses (2.4 nm) and obtained fluorinated flakes with a reduced thickness of 1.5 nm (Figure S1). The

fluorination of mono- and bi-layer InSe resulted in the disappearance of the flakes, indicating an inherent instability of the thinner crystals. It is also noteworthy that thicker layers of InSe preserved their anisotropic structure after fluorination (Figure 1a,b).



**Figure 1. Characterization of fluorinated InSe.** **a**, Optical microscope images of InSe flakes on quartz substrate before (top left) and after (top right) fluorination. Scale bars, 7  $\mu\text{m}$ . **b**, An AFM image of the area marked with the red rectangle in Figure 1a. Scale bar, 5  $\mu\text{m}$ . White curve: height profile along the dashed line. **c**, **and d**, Photographs of bulk InSe before and after the fluorination, respectively. Scale bars, 1 mm. **e**, **and f**, Cross-sectional SEM images of bulk pristine InSe and fluorinated InSe, respectively. Scale bars, 5  $\mu\text{m}$ . **g**, Raman spectra of a fluorinated InSe flake ( $\approx 10$  nm thick), fluorinated bulk InSe, commercial  $\text{InF}_3$ , and pristine bulk InSe. **h**, High angle annular dark field (HAADF) scanning transmission electron microscopy (STEM) image of fluorinated InSe. Scale bar, 5 nm. **i**, Fast Fourier transform (FFT) from the region in Figure 1h, showing  $\{102\}$  and  $\{104\}$  planes in k-space. Scale bar, 2  $\text{nm}^{-1}$ . XPS spectra of bulk fluorinated InSe crystal and commercial  $\text{InF}_3$  powder showing **j**, selenium, **k**, indium, and **l**, fluorine peaks.

Figure 1c,d shows the optical photographs of pristine and fluorinated bulk InSe crystals. The fluorinated bulk crystals are red in colour (Figure 1d), in sharp contrast to bulk InSe which is black (Figure 1c). After fluorination, the crystal becomes harder and brittle compared to the pristine InSe, indicating the loss of layered structure and formation of a covalent crystal. Direct exfoliation of these fluorinated crystals using micromechanical exfoliation was not successful, confirming the covalent nature of the  $\text{InF}_3$  crystal. This is further confirmed by the cross-sectional scanning electron microscopy characterisation shown in Figure 1e,f where a layered to a non-layered transition is apparent after fluorination.

We used Raman spectroscopy, transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS) to characterize the fluorinated samples. The Raman spectrum of bulk InSe shows three characteristic peaks at  $117\text{ cm}^{-1}$ ,  $179\text{ cm}^{-1}$  and  $227\text{ cm}^{-1}$  (Figure 1g) corresponding to the  $A_1'(\Gamma_1^2)$ ,  $E'(\Gamma_3^1) - \text{TO} + E''(\Gamma_3^3)$  and  $A_1'(\Gamma_1^3)$  phonon modes<sup>20</sup>. These peaks are not observed after fluorination. Instead, the fluorinated samples show a peak at  $\approx 250\text{ cm}^{-1}$  with a shoulder at  $232\text{ cm}^{-1}$  and another weaker mode at  $\approx 495\text{ cm}^{-1}$  (Figure 1g and Figure S2). The absence of the InSe Raman peaks and the appearance of new peaks in the Raman spectra suggest complete fluorination of both the bulk InSe and the InSe flakes on quartz. Moreover, similarities between the Raman spectra from the bulk fluorinated crystal and the exfoliated flake suggest similar fluorination chemistry for both types of samples. Due to the relatively high affinity of indium to fluorine, one would expect the most probable outcome of the InSe fluorination to be  $\text{InF}_3$ <sup>21</sup>. High-resolution transmission electron microscopy (HRTEM) of the fluorinated InSe samples is consistent with the  $\text{InF}_3$  atomic structure (Figure 1h,i), with the Fourier transform of the HRTEM image showing the  $\{102\}$  and  $\{104\}$  planes of the  $\text{InF}_3$  crystal ( $R\bar{3}c$  h (167) space group) with lattice spacings of  $3.93\text{ \AA}$  and  $2.854\text{ \AA}$ , respectively<sup>22</sup>. In agreement with this, the selected area

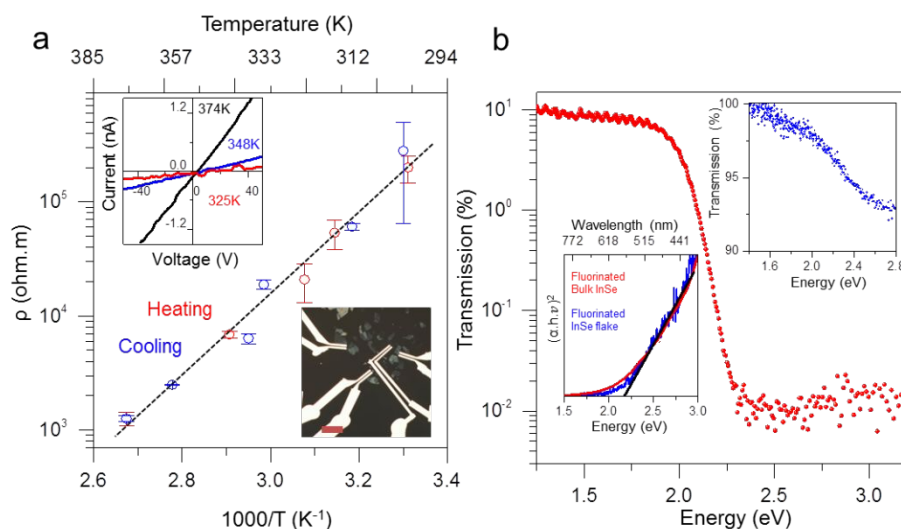
electron diffraction and the X-ray diffraction experiments (Figure S3 and S4) further confirm the expected  $\text{InF}_3$  structure for fluorinated InSe.

It is notable, however, that the Raman spectra for commercial  $\text{InF}_3$  powders were found to be different from those of the fluorinated InSe crystals, indicating that these materials might have a different chemical composition (Figure 1g). The difference in the Raman spectrum of the reference  $\text{InF}_3$  and the  $\text{InF}_3$  obtained by fluorination of InSe is intriguing. To understand this difference, we conducted an XPS analysis of these samples. Figure 1j-l shows XPS from the reference commercial  $\text{InF}_3$  and the  $\text{InF}_3$  obtained by fluorination of InSe. Both samples show indium  $3d_{3/2}$ , and  $3d_{5/2}$  peaks at 453.5 eV and 446 eV, along with the fluorine 1s peak at 685.5 eV, which confirms the covalent  $\text{InF}_3$  atomic structure of the fluorinated samples, in agreement with electron microscopy and X-ray analysis<sup>6</sup>. Furthermore, a closer look of the spectra from the fluorinated InSe reveals a significant amount ( $\approx 2\%$ , see methods) of selenium doping in the crystal (Figure 1j). This doping was absent in the commercial  $\text{InF}_3$  samples (Figure 1j) and could be responsible for the variation in the Raman spectra compared to commercial  $\text{InF}_3$  powder, as discussed below. We have also noticed that the Raman spectrum of Se-doped  $\text{InF}_3$  was not affected by slight changes in the amount of Se doping (Figure S5).

To assess the electronic properties of the Se-doped  $\text{InF}_3$  films, we performed electrical and optical measurements (see methods). Electrical transport measurements were performed on two-terminal devices fabricated with a fluorinated InSe flake ( $\approx 10$  nm thick) on a quartz substrate (see methods). These devices showed a high room-temperature resistivity, typically in the range of  $10^5 \Omega\cdot\text{m}$  (Figure 2a). The temperature dependent electrical resistivity follows an Arrhenius-type behaviour described by the empirical relation

$$\rho = \rho_0 \cdot e^{\left(\frac{E_A}{k_B T}\right)} \quad (1)$$

where  $E_A$  is an activation energy,  $k_B$  is the Boltzmann constant,  $T$  is the temperature in Kelvin, and the parameter  $\rho_0$  is only weakly dependent on  $T$  (Figure 2a)<sup>6, 23</sup>. The fitting of the data (shown in Figure 2a) yields  $E_A = 0.7 \pm 0.1$  eV. The electrical measurements revealed no change in the room temperature resistivity after heating the fluorinated samples in air to temperatures of 100 °C and subsequent cooling down, confirming the thermal stability of the Se-doped  $\text{InF}_3$ .



**Figure 2. Band gap estimation.** **a**, Temperature-dependent electrical resistivity of the fluorinated InSe flake. Top inset: Current-voltage I-V curves at different temperatures (colour coded labels). Bottom inset: optical micrograph of the device. Scale bar, 10  $\mu\text{m}$ . **b**, Optical transmission through fluorinated bulk InSe and fluorinated InSe flake ( $\approx 10$  nm in thickness) on a quartz substrate (top inset) at 300K. Bottom inset: the associated Tauc plots (see methods) indicate a direct bandgap of 2.2 eV for both bulk fluorinated InSe and the fluorinated InSe flake (colour coded labels).

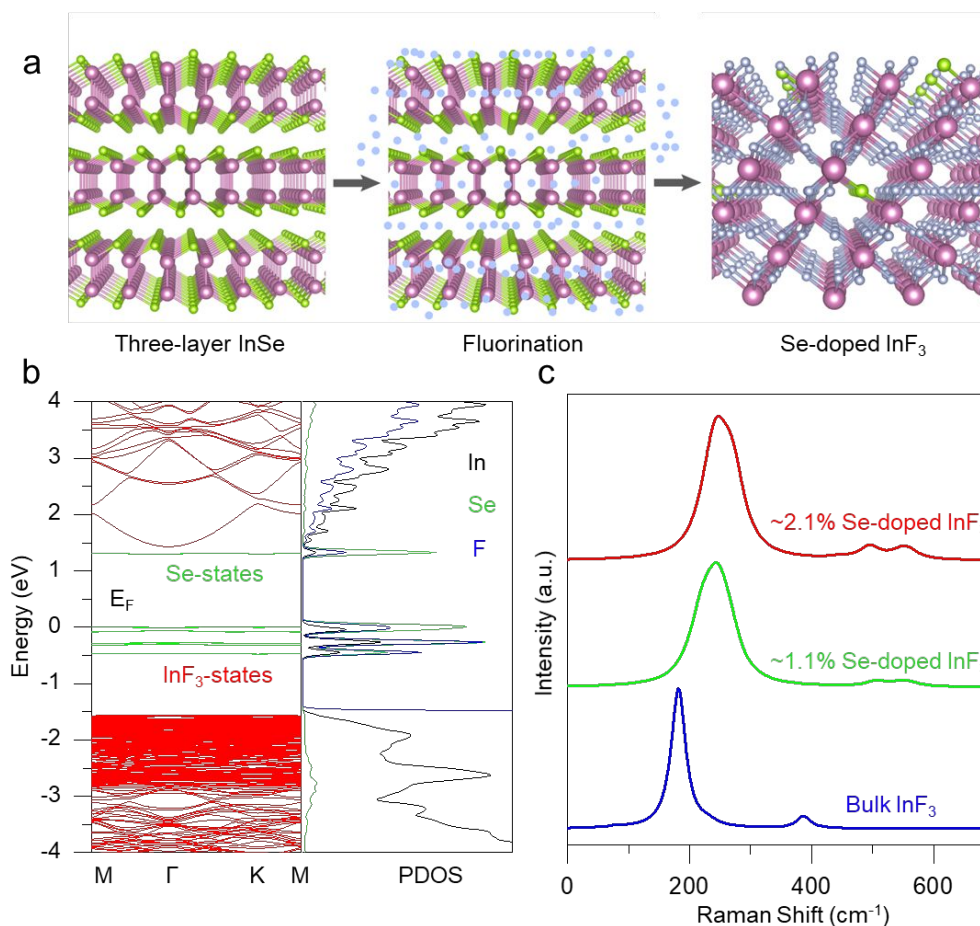
For an intrinsic semiconductor, the activation energy  $E_A$  from the transport measurements would be related to the bandgap energy  $E_g$  of the material, *i.e.*  $E_g/2 = E_A$ . On the other hand, for an extrinsic semiconductor containing impurities and/or defects in the lattice,  $E_A$  would be related to the binding energy and occupancy of the defect/impurity states within the bandgap<sup>6</sup>. To probe the bandgap energy of the fluorinated samples (Se doped  $\text{InF}_3$ ), we performed optical absorption



experiments (see methods). Figure 2b shows the optical transmission spectra of the Se-doped  $\text{InF}_3$  crystals, demonstrating a strong optical absorption above  $\approx 2$  eV. The Tauc plot analysis (Figure 2b bottom inset; see methods) reveals that the Se-doped  $\text{InF}_3$  samples obtained by fluorination of both InSe flakes and bulk crystals have a direct bandgap with  $E_g \approx 2.2$  eV<sup>3</sup>. This value is significantly larger than the energy  $2E_A = 1.4$  eV derived from the electrical measurements, suggesting that the chemical potential is pinned on mid-gap impurity states. We have also investigated the photoluminescence of the Se-doped  $\text{InF}_3$ , but no emission was observed, consistent with the presence of non-radiative recombination centres, as was reported earlier for fluorographene<sup>6</sup>. We also calculated the optical constants of the Se-doped  $\text{InF}_3$ , which showed an almost constant real refractive index of 2, while the imaginary part of the refractive index reduced to near zero for wavelengths  $> 600$  nm (Figure S6). This implies that Se-doped  $\text{InF}_3$  transmits all wavelengths above 600 nm with near zero attenuation.

To further understand the fluorination of InSe, we performed *ab-initio* Density Functional Theory (DFT) calculations (see methods). Our structure optimization and phonon dispersion calculations show that a minimum of three layers of InSe is essential for the formation of  $\text{InF}_3$  crystal by fluorination of InSe (Figure S7). Fewer than three layers of fully fluorinated InSe were dynamically unstable and did not structurally converge into  $\text{InF}_3$ , in agreement with the experimental findings. Figure 3a shows a schematic diagram of the chemical conversion of 3 layers of InSe into Se-doped  $\text{InF}_3$ . Electronic band dispersion calculations reveal that bulk  $\text{InF}_3$  is a wide gap semiconductor with a bandgap of 2.9 eV (Figure S8). The doping of  $\text{InF}_3$  with Se results in impurity mid-gap states, which significantly decreases the band gap of  $\text{InF}_3$  to  $\approx 2.2$  eV, as observed in the experiment. As shown by the green bands in Figure 3b, the impurity mid-gap states arise almost entirely from the Se orbital states, giving rise to a smaller bandgap in Se-doped  $\text{InF}_3$ . Also,

as shown in Figure 3b, the band dispersions (red bands) of both the valence band and the conduction band edges of  $\text{InF}_3$  are mostly dominated by the F- $p$  orbitals, with the In- $d$  orbitals also contributing to the valence band edges.



**Figure 3.** *Ab-initio* density functional theory calculations. **a**, Schematic showing the fluorination of three-layer InSe to  $\text{InF}_3$ . Purple, light blue, and green spheres corresponds to indium, fluorine, and selenium, respectively. **b**, Electronic-band structure and the corresponding partial density of states (PDOS) for 2.1% Se-doped  $\text{InF}_3$  (color-coded labels). The green bands represent Se states. The midgap fluorine and indium states are absent in the pristine  $\text{InF}_3$  (Figure S8) and only introduced after Se doping. The Fermi energy is set to 0 eV. **c**, Calculated Raman spectrum of bulk  $\text{InF}_3$  and Se-doped  $\text{InF}_3$  at two different doping levels.

We also modelled the vibrational spectrum of  $\text{InF}_3$  and Se-doped  $\text{InF}_3$ , and found that Se-doping modifies the Raman spectrum of  $\text{InF}_3$ , consistent with the experimental results. The calculated Raman spectrum of both  $\text{InF}_3$  and Se-doped  $\text{InF}_3$  (Figure 3c) agrees well with the experimentally

recorded spectrum (see supplementary text 1). We have also noticed that the calculated Raman spectrum of Se-doped  $\text{InF}_3$  was not affected by slight changes in the amount of Se doping as seen in experiment (Fig. 3c and Figure S5).

To demonstrate the scalability of our synthesis procedure, we prepared large area Se-doped  $\text{InF}_3$  by fluorinating liquid-exfoliated InSe laminates (see methods and Figure S9 and S10). Liquid exfoliated InSe flakes ( $\approx 2.5$  nm thick) were obtained by ultra-sonication of InSe powder in Isopropyl Alcohol<sup>24,25</sup>. These nanosheets were filtered onto an Anodisc alumina/PTFE membrane and fluorinated at 350 °C for 48 hrs. The resulting  $\text{InF}_3$  films show structural and optical characteristics similar to Se-doped  $\text{InF}_3$  obtained by the fluorination of mechanically exfoliated InSe (Figure S10).

In conclusion, we have successfully demonstrated the synthesis of atomically thin covalent crystals by chemical conversion of a few-layered van der Waals material. This is achieved by synthesizing atomically thin Se-doped  $\text{InF}_3$  by fluorinating few-layer InSe flakes. The resulting Se-doped  $\text{InF}_3$  was found to be a semiconductor with an optical band gap of  $\approx 2.2$  eV. The experimentally observed Raman spectra and bandgap match the calculated values. Our approach could be used to synthesize a large variety of other 2D covalent solids, which cannot be produced by exfoliation.

## Methods:

**Fluorination of InSe flakes:** InSe flakes were prepared on a quartz wafer using micromechanical exfoliation of Bridgman-grown bulk  $\gamma$ -InSe crystals. Quartz substrates of size ( $\approx 5$  cm x 5 cm) were cleaned using acetone and isopropyl alcohol for 10 min each, followed by  $\text{O}_2/\text{Ar}$  plasma cleaning for 10 min. The substrates were immediately transferred inside a glove box for mechanical

exfoliation of InSe crystals under argon environment with H<sub>2</sub>O and O<sub>2</sub> levels less than 0.1 ppm. The transferred crystals on quartz were then taken to a PTFE container mixed with excess XeF<sub>2</sub> crystals and heated to 100 °C on a hot plate for 48 hrs. After fluorination the sample was then annealed at 80 °C for 12 hrs inside a glove box to remove residual XeF<sub>2</sub> crystals and used for subsequent measurements.

**Fluorination of bulk InSe:** A small piece of InSe crystal was scrapped off a large crystal using a surgical blade inside a glove box. The crystal was then mixed with excess (~ 100 times by mass) XeF<sub>2</sub> inside a PTFE lined stainless steel container and heated to 350 °C for 48 hrs on a hot plate. The crystals thus obtained were annealed at 150 °C for 12 hrs inside a glove box to remove the residual XeF<sub>2</sub> crystals and used for subsequent measurements.

**Preparation and fluorination of InSe laminates:** InSe powder for liquid exfoliation was purchased from Chengdu Alfa Metal Material Co.,Ltd, China and used as received. 10 mg of InSe powder was dispersed in about 100 ml of iso-propyl alcohol. The dispersion was then sonicated for 12 hrs. The resulting dispersion after sonication was centrifuged at 4000 rpm for 10 min. The supernatant was collected and filtered through a PTFE (0.1 µm pore size and 47 mm diameter, purchased from Sterlitech) or Anodisc alumina membrane (0.2 µm pore size and a diameter of 47 mm, purchased from Millipore) to obtain InSe laminates with thickness of a few microns. These laminates were fluorinated at 350 °C on a hot plate in a PTFE-lined autoclave for 48 hrs and characterised using X-ray diffraction. After the fluorination, the InF<sub>3</sub> coating was loosely attached to the PTFE/alumina substrate and could be peeled from the substrate to obtain freestanding films of InF<sub>3</sub> (Figure S10).

**AFM measurements:** AFM imaging was performed using a Bruker Dimension FastScan AFM operating in peak force tapping mode.

**Raman measurements:** We used HORIBA's Raman spectrometer (XploRA PLUS) with a laser excitation of 532 nm (spot size  $\sim 1\ \mu\text{m}$ , laser power of 1.35 mW and spectrometer grating of 1200 grooves per millimetre) for measuring the Raman spectra of the samples.

**TEM measurements:** Samples for TEM were prepared by rubbing  $\text{InF}_3$  bulk crystals against a TEM grid (metal mesh). We used an FEI Titan G2 80-200 S/TEM 'ChemiSTEM' operated at 200 kV. Imaging was carried out in HAADF STEM mode, with a probe current of 180 pA and convergence angle 21 mrad, while diffraction was performed in TEM mode.

**X-Ray Diffraction measurements:** X-ray diffraction (XRD) was performed using a Rigaku SmartLab XRD with  $\text{Cu K}\alpha$  radiation (medium resolution parallel beam measurement mode,  $\lambda = 1.5406\ \text{\AA}$ ) with a step size of 0.01 degrees. The crystals were pressed and made into a powder using a mortar before placing into the X-ray sample holder. The voltage and current of the X-ray tube was fixed to 40 KV and 45 mA, respectively. XRD from liquid exfoliated InSe before and after fluorination was obtained directly from the as-prepared samples.

**XPS measurements:** XPS analysis was performed with a Kratos AXIS Ultra DLD apparatus, equipped with a monochromated  $\text{Al K}\alpha$  radiation X-ray source, a charge neutralizer, and a hemispherical electron energy analyser. During data acquisition, the chamber pressure was kept below  $10^{-9}$  mbar. The spectra were analysed using the CasaXPS software pack and corrected for charging using C 1s binding energy as the reference at 284.8 eV. Survey scans and high-resolution scans were carried out at pass energies of 80 eV and 20 eV, respectively. Atomic percentage of elements were calculated from the survey scans using CasaXPS software pack.

**Electrical measurements:** Electrical measurements of  $\text{InF}_3$  crystals were conducted using a 2400 Keithley source meter. The temperature-dependent conductivity studies were conducted by heating

a device in air using a hot plate. The temperature on the surface of the sample was measured using an infrared thermometer.

**Optical measurements:** Wavelength-dependent transmission of  $\text{InF}_3$  samples was measured using a homemade spectrometer with focusing optics in transmission mode. The incident light from a laser driver light source (LDLS) was focused on the sample with the FL 40x objective and then collected using a similar objective. The transmitted light was focused on the entrance of an optical fiber (200  $\mu\text{m}$  core) coupled to the Ocean Optics USB2000 spectrometer. The transmission spectra were obtained by normalizing the spectra measured from the sample with respect to the spectra measured from the substrate. We extracted the spectral dependencies of the complex refractive index using spectroscopic ellipsometry. The ellipsometric measurements were performed with a Woollam VASE variable angle ellipsometer (M-2000F) with a focal spot of just 30  $\mu\text{m}$  in the wavelength range of 240–1700 nm. The ellipsometric data were modelled with WVASE32 software based on Fresnel coefficients for multilayered films.

**Bandgap calculations:** To probe the optical band gap of the Se-doped  $\text{InF}_3$  crystals, we used the measured absorption coefficient (Figure S6) to construct Tauc plots. The optical absorption strength depends on the difference between the photon energy and the bandgap as

$$(\alpha h\nu)^{1/n} = A(h\nu - E_g) \quad (2)$$

where  $h$  is Planck's constant,  $\nu$  is the photon's frequency,  $\alpha$  is the absorption coefficient,  $A$  is proportionality constant, and  $E_g$  is the bandgap.  $E_g$  is obtained from the X-intercept of the linear regime of the Tauc plot  $[(\alpha h\nu)^{1/n} \text{ vs. } h\nu]$ . The nature of the transition is denoted by the value of  $n$ , where  $n = \frac{1}{2}, \frac{3}{2}, 2$  or  $3$  for direct allowed, direct forbidden, indirect allowed, and indirect forbidden

transitions, respectively. For our samples,  $n = \frac{1}{2}$  provided the best linear regime in the Tauc plot (Figure 2b inset).

**DFT-methodology:** For the investigation of the structural, electronic, and vibrational properties of bulk InSe and doped InF<sub>3</sub> crystals, density functional theory (DFT)-based first principle calculations were performed as implemented in the Vienna ab-initio simulation package (VASP)<sup>26</sup>. The Perdew-Burke-Ernzerhof (PBE) form of generalized gradient approximation (GGA) was adopted to describe electron exchange and correlation<sup>27</sup>. In order to take into account strong correlations between In-*d* orbital electrons, The DFT+U method was used<sup>28</sup>. The effective on-site Coulomb parameter,  $U_{\text{eff}}$ , was taken to be 7 eV.

The kinetic energy cutoff for plane-wave expansion was set to 500 eV and the energy was minimized until its variation in the following steps became less than 10<sup>-8</sup> eV. The width of the Gaussian smearing was chosen to be 0.05 eV for both geometry optimizations and partial density of states (PDOS) calculations. For the vibrational spectrum of each bulk structure, first-order off-resonant Raman activities were calculated at the  $\Gamma$  point of the Brillouin Zone (BZ). Firstly, the zone-centered phonon modes were calculated using small-displacement methodology as implemented in VASP. Then using the vibrational characteristic of each optical phonon mode, the derivative of macroscopic dielectric tensor was calculated with respect to each normal vibrational mode to obtain the corresponding Raman activity<sup>29, 30</sup>.

## ASSOCIATED CONTENT

### Supporting Information

The following files are available free of charge on the ACS Publications website.

Calculated Raman spectrum of  $\text{InF}_3$  and Se doped  $\text{InF}_3$ , Atomic Force Microscopy (AFM) Image of thin  $\text{InF}_3$  crystals, Raman spectrum of fluorinated  $\text{InSe}$  over an extended range of wavenumbers, Selected Area Electron Diffraction (SAED) and X-Ray Diffraction (XRD) pattern of fluorinated  $\text{InSe}$ , XPS and Raman spectra from  $\text{InF}_3$  with different Se doping levels, Optical characterization of  $\text{InF}_3$ , Phonon dispersion curve for thin  $\text{InF}_3$  structures, Bandstructure of  $\text{InF}_3$ , characterization of liquid exfoliation of  $\text{InSe}$  nanosheets, and large area  $\text{InF}_3$  film.

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Notes: The authors declare no competing financial interest.

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